Supporting Information for

Corygaline A, Hexahydrobenzophenanthridine Alkaloid with Unusual Carbon Skeleton from *Corydalis bungeana* Turcz.

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List for Supportting Information

General experimental procedures

Optical rotations were measured on a JASCO DIP-370 digital polarimeter. Infrared spectra were recorded on a Bruker IFS-55 spectrometer. UV spectra were measured using a Shimadzu UV-1700 spectrophotometer. CD spectra were obtained using MOS 450 detector from BioLogic in the 200-400 nm wavelength range. 1D and 2D NMR spectra were measured on Bruker DPX-400 instrument. All ^{1}H and ^{13}C NMR chemical shifts (δ) are presented in ppm relative to the TMS signal at 0.00 ppm as internal reference, and the coupling constants (J) are given in Hz. HRESIMS were obtained on a MicroTOF spectrometer (Bruker Co., Karlsruhe, Germany) . Column chromatography was performed on silica gel (200-300 mesh, Qingdao Marine Chemical Inc., Qingdao, China), MCI gel (CHP20P, 75-150 μM, Mitsubishi Chemical Industries Ltd.), and ODS (YMC, Kyoto, Japan). Semipreparative HPLC was carried out on a Shimadzu LC-6AD binary pump system with a Shimadzu SCL-10Avp detector (210 nm) using a Diamonsil C18 (250 × 10 mm, 10 μm) column. TLC analysis (analytical and preparative) was performed using precoated silica GF254 (Qingdao Marine Chemical Inc., Qingdao, P. R. China) plates, and spots were visualized by exposure under UV254/365 light, by spraying with Dragendorff's reagent.

Plant material

The plants of *Corydalis bungeana* Turcz. were collected in Hebei, China, in September 2014 and identified by Professor Jiuzhi Yuan from the Department of Traditional Chinese Materia Medica, Shenyang Pharmaceutical University. A voucher

specimen (No. 201401) is deposited in the the Nature Products Laboratory of Shenyang Pharmaceutical University, Shenyang, P. R. China.

Extraction and isolation

The aerial parts of *Corydalis bungeana* Turcz. (50 kg) were extracted with 75% EtOH (2 × 150 L, 1h) at room temperature. After evaporation of the solvent, the EtOH extract was suspended in H_2O (20 L) and extracted with CH_2Cl_2 (30 L). The CH_2Cl_2 extract (300 g) was subjected to silica gel CC, eluting with gradient mixtures of CH_2Cl_2-MeOH (1:0-0:1 gradient system), to give fractions A-C. Fraction A (132 g) was subjected to MCI gel column chromatography with a H_2O/MeOH (6:4, 4:6, 2:8, 0:10, v/v) gradient system to give fractions A1-A4. Fraction A3 was separated using silica gel (petroleum ether- acetone, 1:0-0:1 gradient system), RP-18 (H_2O-MeOH, 3:7 to 0:1, v/v), and semipreparative HPLC (MeOH-H_2O; 35:65, v/v; flow rate, 2.0 mL/min) to yield compounds **1** (4.3 mg, t_R 48.2 min)

Anti-inflammatory Bioassay

Mouse monocyte-macrophage RAW264.7 cells were used in the anti-inflammatory assay. Cell culture, Griess, and MTT procedures and data analysis for the inhibition of NO production assay were the same as in the published protocol. The cells were cultivated at 37 °C in RPMI 1640 medium containing 10% heat-inactivated fetal bovine serum (Gibco, USA), 100 U/mL of penicillin and 100 lg/mL of streptomycin in a humidified atmosphere containing 5% CO_2. The cell lines were seeded in 96-well plates with 1×10^4 cells/well and allowed to adhere for 24 h at 37 °C in 5% CO_2. Then the cells were pretreated with various concentrations of test compounds for 2 h.

and activated with 1 μg/mL of LPS for 24 h. Minocycline (IC_{50} = 31.28 μM) was used as a positive control. The Griess reagent was used to determine NO production by measuring the accumulation of nitrite in the culture supernatant. The colour density was measured at 540 nm using a microplate reader (Molecular Devices, USA). Experiments were performed in triplicate.

Physical constants and spectral data of 1

Corygaline A (**1**): white, amorphous powder; $[\alpha]^{20}_{D}$ +87.0 (c 0.1, MeOH); UV (MeOH) λmax (log ε) 289 (3.84) nm; IR (KBr) ν_{max} 3433, 2985, 2923, 1630, 1492, 1398, 1369, 1269, 1173, 1005, 799 cm^{-1}; positive HRESIMS $[M + H]^+$ m/z 382.1313 (calcd for $C_{21}H_{19}O_6N$, 382.1285); ^1H NMR data and ^{13}C NMR data, see Table 1.

Experimental vs GIAO NMR shift of compound 1

position	exp	A	B
1	106.7	110.8	114.0
2	146.4	157.1	153.9
3	149.5	153.2	153.6
4	115.3	121.7	108.2
4a	120.9	130.7	140.7
6	65.9	73.0	67.9
6a	113.7	121.9	123.0
7	142.7	150.9	151.4
8	146.8	154.9	154.3
9	118.1	111.9	112.2
10	108.1	123.8	127.6
10a	132.4	143.1	142.8
11	75.9	82.9	98.3
12	31.8	37.1	48.2
12a	128.6	139.0	150.0
13	41.3	48.9	55.4
14	75.3	83.7	81.0
15	86.5	93.5	134.9
13-CH_3	20.6	23.1	28.1
OCH_2O	101.4	107.9	107.8
	102.2	108.5	110.0
RMSD		8.12	15.85

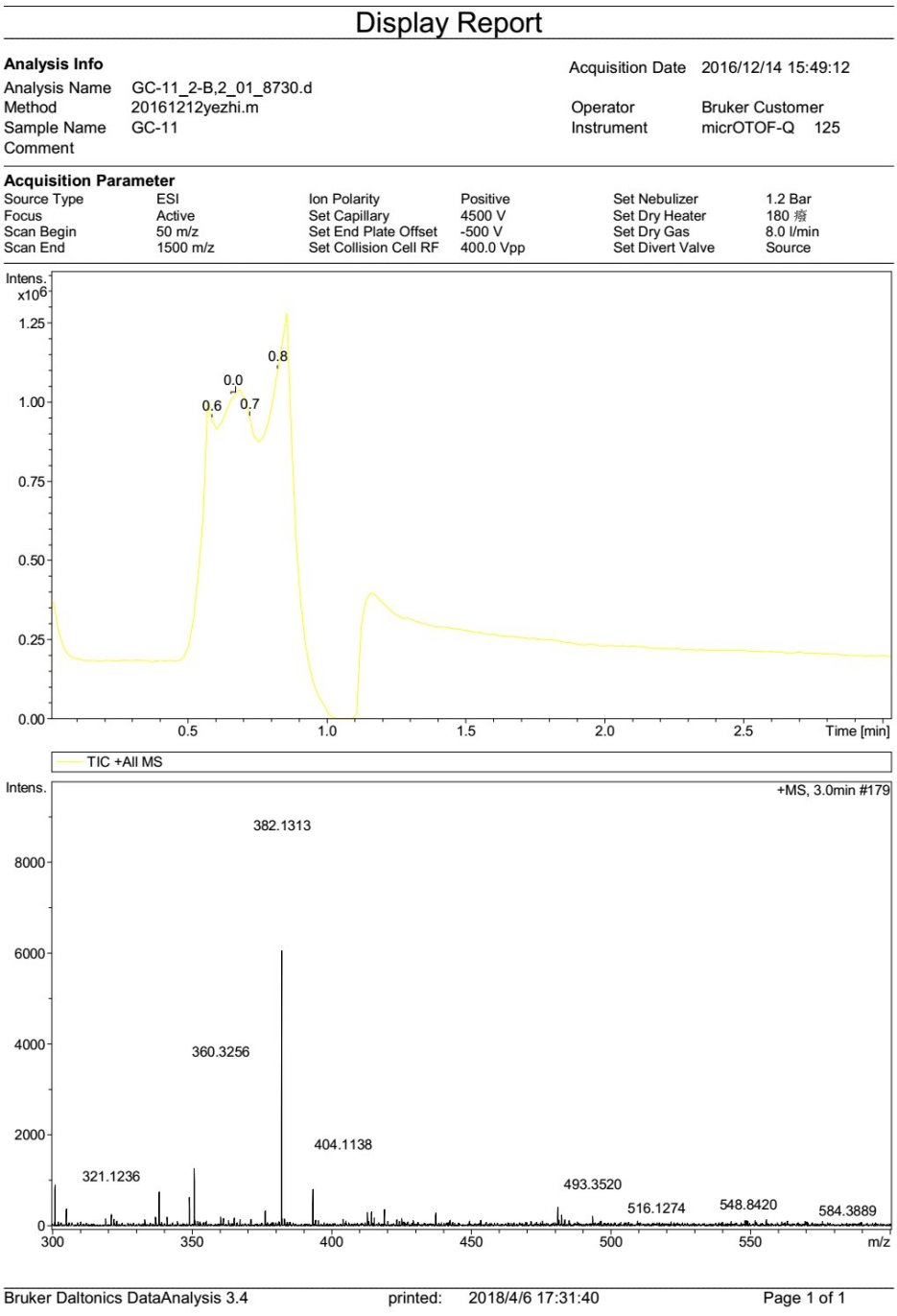

Figure S1. HR-ESI/MS spectrum of compound **1**

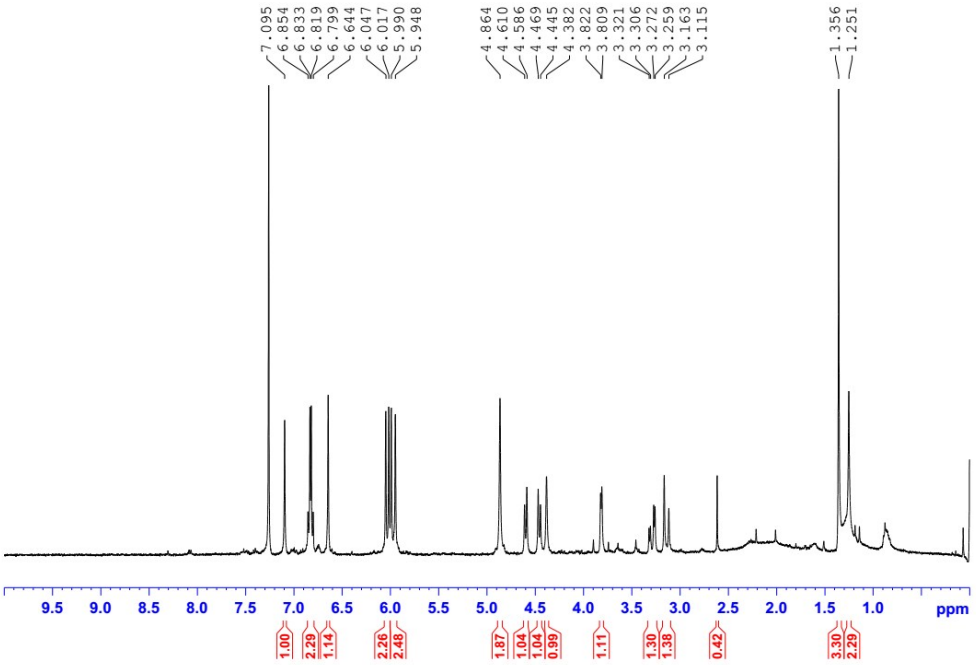

Figure S2. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1**

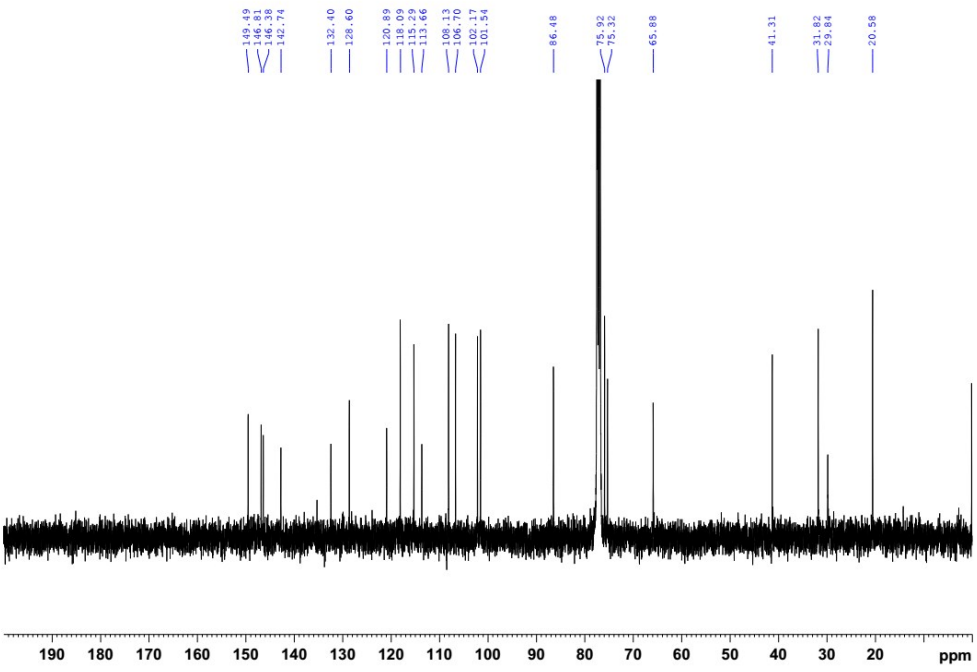

Figure S3. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **1**

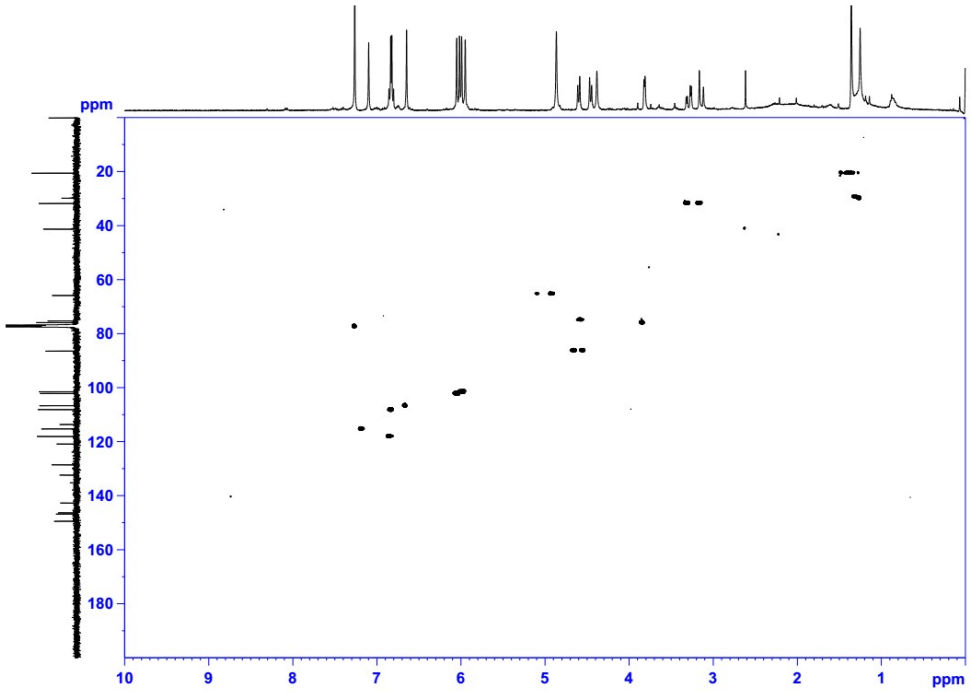

Figure S4. HSQC spectrum of compound **1**

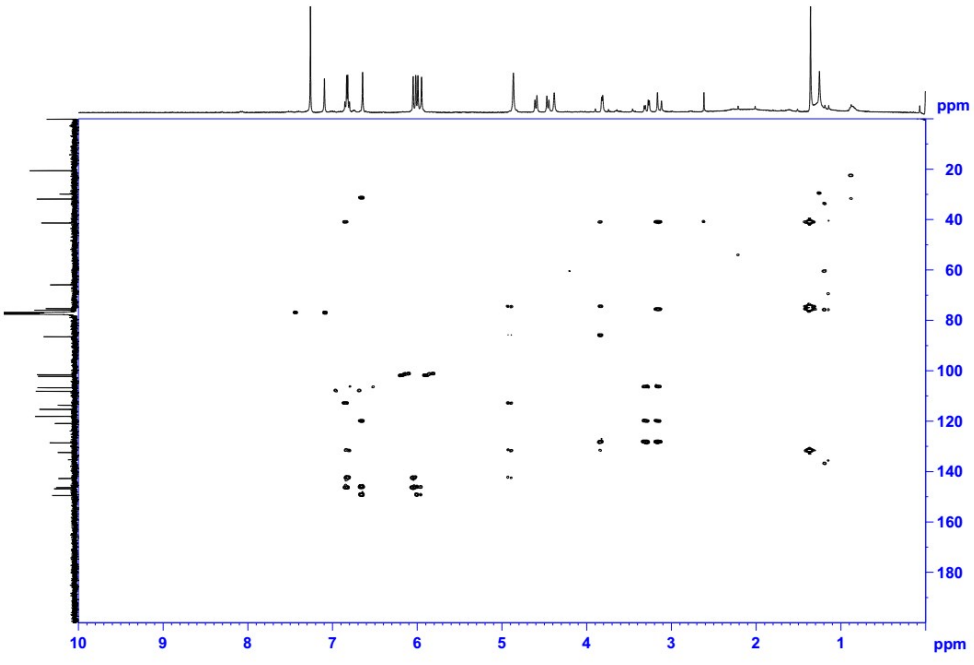

Figure S5. HMBC spectrum of compound **1**

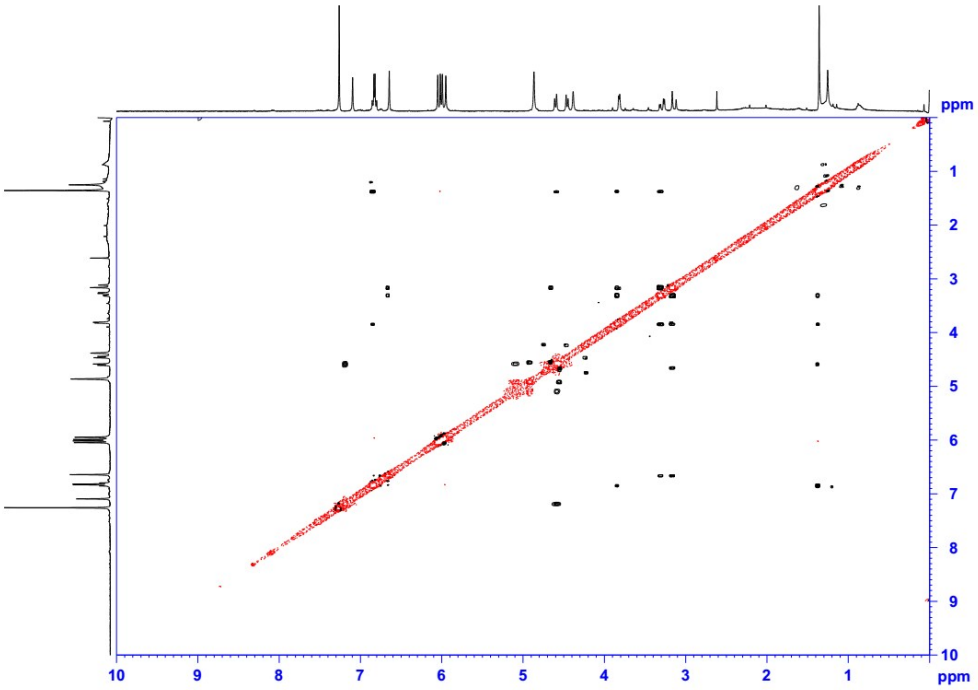

Figure S6.NOESY spectrum of compound **1**